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Ethylene Vinyl Alcohol Copolymer (EVOH) Resins

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57.1 Polymer

Ethylene vinyl alcohol (EVOH) resins are hydrolyzed copolymers of vinyl acetate and ethylene. The vinyl alcohol base has exceptionally high gas barrier properties, but it is water soluble and difficult to process. By copolymerizing ethylene with vinyl alcohol, the high gas barrier properties are retained and significant improvements are achieved in moisture resistance and processibility.

A typical reaction for producing EVOH resins is shown on page 57-3. Under proper conditions, this reaction yields a copolymer that is more than 99% hydrolyzed.

Table 57.1 lists the range of EVOH resins presently available.

57.2 Barrier Properties

EVOH copolymers are highly crystalline, and their properties are highly dependent on the relative concentration of the comonomers. Generally speaking, as the ethylene content increases, the gas barrier properties decreases, the moisture barrier properties improve, and the resins are processed more easily (see Table 57.2).

The presence of a hydroxyl group in the molecular chain renders the gas barrier properties of the EVOH resins sensitive to moisture. As the moisture content of the resin increases, the gas barrier properties decrease. However, by proper use of companion materials in a multilayer structure, this effect can be minimized.

Table 57.3 shows how the combination of different materials can be used to minimize the moisture content of the EVOH and maintain superior gas barrier properties. In this article, any aqueous-based food is considered to be 100% relative humidity; the storage environment is shown at relative humidities of 65 and 85%.

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TABLE 57.1 Properties of Ethylene Vinyl Alcohol Resins

Property	Range
Melt index	0.7–15.0 g/10 min
Density	1.12–1.21 g/cm^3
Melting point	156–191°C
Crystalline temperature	134–167°C
Ethylene content	27–48 mol%

TABLE 57.2 Barrier Properties

EVOH (mol% Ethylene)	Gases[a]				Moisture[b]
	O_2	CO_2	N_2	He	
27	0.01	0.04		7.7	6.8
32	0.02	0.05	0.002	15.5	3.8
38	0.03	0.10	0.003	25.5	2.1
44	0.07	0.20	0.005	40.0	1.4
48	0.11	.032	0.007	52.0	1.4

[a] In cubic centimeter-mils per 100 in.^{2} 24 hours per atm at 20°C and 65% relative humidity.
[b] In gram-mils per 100 in.^{2} 24 hours per atm 40°C and 90% relative humidities.

TABLE 57.3 Oxygen Transmission (O_2TR) Rate versus Barrier Layer Relative Humidity

Film Structure[a]				Inside Package			
				Outside (65%RH)		Outside (85%RH)	
Outside: 0.8 mil	Barrier: 0.6 mil	Inside: 2 mils	Temperature (°C)	RH of Barrier (%)	O_2 TR[b] (Barrier %)	RH of Barrier (%)	O_2 TR[b] (Barrier %)
PP	27 mol% EVOH	LLDPE	5	79	0.03	88	0.05
			20		0.04		0.10
PP	27 mol% EVOH	PP	5	75	0.02	86	0.04
			20		0.03		0.07
PET	27 mol% EVOH	PP	5	72	0.02	84	0.04
			20		0.03		0.07
Nylon	32 mol% EVOH	LDPE	5	67	0.01	81	0.02
			20		0.03		0.05
PP	32 mol% EVOH	LDPE	5	79	0.05	88	0.05
			20		0.04		0.12
PS	44 mol% EVOH	LDPE	5	70	0.05	83	0.05
			20		0.17		0.27

[a] PP, polypropylene; PET, polyethylene terephthalate; PS, polystyrene.
[b] In cm^3 per 100 in^2 per 24 hours per atm.

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TABLE 57.4 Flavor Barrier Data (Citrus and Tropical Flavors)[a]

Film[b]	Thickness (μm)	Duration					
		1 h	2 h	15 h	1 Day	4 Days	35 Days
EVOH-32	15	A	A	A	A	A	A
EVOH-44	15	A	A	A	A	A	A
BO EVHO	15	A	A	A	A	A	A
BO Nylon	15	A	A	B	B	B	B
OPP	20	B	B	C	C	C	C
PVDC	25	A	A	B	B	B	B
LDPE	50	D	D	D	D	D	D

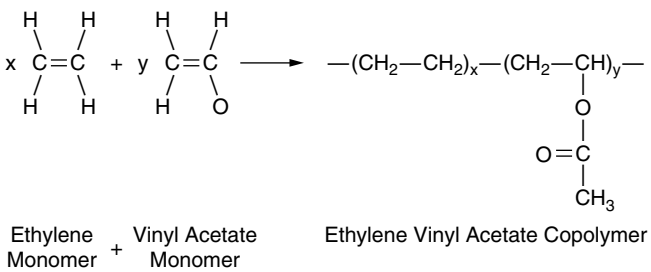
[a] Key: A, no detection; B, faint flavor; C, partial flavor; D, flavor clearly distinguished.
[b] BO EVOH, biaxially oriented EVOH; BO Nylon, biaxially oriented nylon; OPP, oriented polypropylene; PVDC, polyvinylidene chloride; LDPE, low density polyethylene.

TABLE 57.5 Flavor, Aroma, and Solvent Barrier Properties[a]

Resin[b]	Allyl Sulfide: Garlic-Food Type (Croutons, Snacks, Salad Dressins)	Acetic Acid Vinegar-Food Type (Cheddar Cheese, Snacks, Condiments)	Ethylene Acetate: Laminating Adhesive Solvent Residual	Toluene: Printing Ink Solvent Residual	Methyl Ethyl Ketone Printing Ink Solvent Residual
HDPE-Nylon-EVa	0.00008	0.92	0.03	0.02	0.005
HDPE-EVOH-EVA	0.00075	0.035	0.0043	0.007	0.035
PVDC-PP-PVDC	0.0068	1.98	0.34	0.22	3.09
OPP-HDPE-EVOH-EVA	0.00076	1.40	0.15	0.00003	0.09
EVA-Glassine-PVDC	0.50	4.18	6.47	3.15	15.1

[a] g/24 h, m^2, 100 pm at 70°F.
[b] HDPE, high-density polyethylene; EVA, ethylene vinyl acetate; PVDC, polyvinylidene chloride; OPP, oriented polypropylene.

In addition to being outstanding as barrier properties, EVOH resins offer excellent barriers to a variety of flavors, aromas, and solvents (see Table 57.4 and Table 57.5).



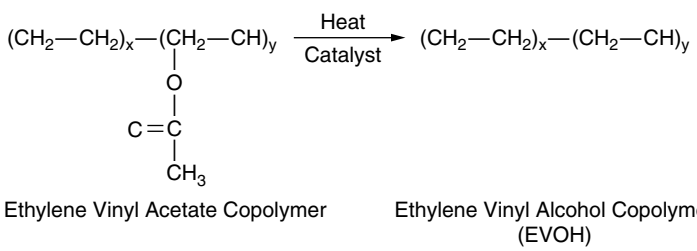


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TABLE 57.6 Properties of Three Commerical Resins

Property	Eval EVOH Resin Grade		
	F101	H101	E105
Maximum service temperature °C	240	240	250
Melting point °C	181	175	164
Glass transition temperature °C	69	62	55
Tensile strength, psi	11,220	9,400	8,520
Tensile yield strength, psi	10,365	8,300	7,385
Elongation at break, %	230	280	280
Young's modulus, psi	385,000	345,000	298,000
Ethylene content, mol%	32	38	44

TABLE 57.7 Barrier Applications

Fabrication Process	Application	Structure[a]
Lamination or extrusion coating	Food kits, pouches, dry mixes, snacks	BOB/barrier/LLDPE Nylon/PET/barrier/LDPE OPP/barrier/LDPE Paper/HDPE/barrier/EVA
Coextrusion coating	Aseptic packaging Juices and other drink products	LDPE/Paper/barrier/PP/Surlyn LDPE/Paper/LDPE/BARRIER LDPE/Paper/LDPE/barrier LDPE/Barrier

[a] BON, biaxially oriented nylon; LLDPE, linear low-density polyethylene; PET, polyethylene terephthalate; LDPE, low-density polyethylene; OPP, oriented polyethylene; HDPE, high-density polypropylene; EVA, ethylene vinyl acetate; PP, polypropylene.

It is these exceptional barrier properties that permit the use of extremely thin layers of EVOH resins in coextrusion-coated structures for gable top drink cartons, single-serve drink cartons, dry mixes, etc.

In addition to excellent barrier properties, EVOH resins have very good mechanical and thermal properties (see Table 57.6).

57.3 Regulatory Approval

EVOH resins meet U.S. Food and Drug Administration requirements for direct food contact as specified in The Code of Federal Regulations (21 CFR, Section 177.1360), issued September 21, 1982, for all temperatures through 100°C. The use of EVOH resins as an indirect food contact layer also meets the FDA requirement for high temperature retort applications.

Table 57.7 lists packaging structures produced using various fabrication methods.

When using EVOH resins in multilayer structures, it is necessary to use an adhesive to gain adequate bonding strength to the other polymers or substrates. Commercially available adhesive resins such as Plexar, Admer, Modic, or Bynel are suitable for use with EVOH resins. EVOH resins are produced domestically by EVAL Company of America (EVAL reins) and E. I. DuPont (Selar OH resins).

57.4 Fabrication Methods

There are three basic methods of using EVOH to provide the barrier layer in multilayered structures. These are as follows:

- Using them for coextruded structures in which EVOH resins are combined with polyolefins or polyamides to form the structure

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- Using EVOH films that are laminated to other substrates or coated with other materials
- Coating various substrates or monolayer containers with EVOH resins

Generally speaking, coextrusion or lamination is used for structures in which the EVOH layer must be protected from the effects of moisture. When packaging aqueous-based products (tomato ketchup, barbeque sauce, etc.), various combinations of less costly polyolefins are used to provide structural strength and to prevent excess moisture from reaching the EVOH barrier layer and lowering gas barrier properties.

Coating techniques can also be used to produce multilayered structures by the use of either multiple coatings or coextrusion coating. The resulting structure will be very similar to a coextruded structure.

Spray, dip, and/or roller coating of EVOH resins are used to produce containers for carbonated beverages or to establish a barrier to solvents, aromas, or odor. Manufacturers of such products include Kuraray Company Ltd. (Eval resins) and Nippon Gohsei (Soarnol resins) in Japan and Solvay (Clarene resins) in Europe.

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